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LDRD-LW Final Report: 07-LW-041 "Magnetism in Semiconductor Nanocrystals: New Physics at the Nanoscale"

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“Magnetism in Semiconductor Nanocrystals: New Physics at the Nanoscale”

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Introduction

The work conducted in this project was conducted with the aim of identifying and understanding the origin and mechanisms of magnetic behavior in undoped semiconductor nanocrystals (NCs), specifically those composed of CdSe. It was anticipated that the successful completion of this task would have the effect of addressing and resolving significant controversy over this topic in the literature. Meanwhile, application of the resultant knowledge was expected to permit manipulation of the magnetic properties, particularly the strength of any magnetic effects, which is of potential relevance in a range of advanced technologies.

More specifically, the project was designed and research conducted with the goal of addressing the following series of questions:

- (1) How does the magnitude of the magnetism in CdSe NCs change with the organic molecules used to passivate their surface the NC size? i.e. Is the magnetism an intrinsic effect in the nanocrystalline CdSe (as observed for Au NCs) or a surface termination driven effect?
- (2) What is the chemical (elemental) nature of the magnetism? i.e. Are the magnetic effects associated with the Cd atoms or the Se atoms or both?
- (3) What is/are the underlying mechanism(s)?
- (4) How can the magnetism be controlled for further applications?

To achieve this goal, several experimental/technical milestones were identified to be fulfilled during the course of the research:

- (A) The preparation of well characterized CdSe NCs with varying surface termination
- (B) Establishing the extent of the magnetism of these NCs using magnetometry (particularly using superconducting interference device [SQUID])
- (C) Establishing the chemical nature of the magnetism using x-ray magnetic circular dichroism (XMCD) – the element specific nature of the technique allows identification of the element responsible for the magnetism
- (D) Identification of the effect of surface termination on the empty densities of states (DOS) using x-ray absorption spectroscopy (XAS), with particular emphasis on elucidating small changes in the *d*-electron count. Characterizing changes in the *d*-electron density can yield important insight into the mechanisms of magnetism in materials.

As the three attached manuscripts illustrate (presented in preprint form to ensure no infringement of copyright), each of these milestones was successfully illustrated and the results published in the scientific literature during the course of the project. The research team members were able to determine, from a series of XAS, XMCD and SQUID magnetometry measurements, that CdSe NCs are paramagnetic and that the magnitude of magnetic susceptibility is dependent upon the type of organic molecule used to passivate the NC surface (i.e. the observed magnetism results, at least in part, from a surface effect that is not intrinsic to the NCs). In addition, they identified that the mechanism by which the magnetic susceptibility is modified – via π back-donation of *d*-electrons to the organic ligands from the Cd atoms. These findings demonstrate that the magnetic properties are related to the surface Cd atoms and illustrate the means by which the magnetic behavior can be manipulated for specific technological applications. Two of the papers published during the course of the LW project do not contain magnetometry data, but focus on the evolution in electronic structure of the CdSe NCs as a function of particle size. These measurements were crucial in developing an understanding of the electronic behavior of the NCs and, ultimately, in assigning the π back-donation mechanism for inducing controllable paramagnetic behavior.

Significantly, the research team has also filed a patent application based upon their research: “Method for Creating Ligand Induced Paramagnetism in Nanocrystalline Structures” Docket: IL-11858.

It is noted that both LDRD-LW and Office of Basic Energy Sciences (OBES) funding is acknowledged in the attached manuscripts. As such, is important to indicate that funds were not comingled during the course of the project. Some of the experimental data presented in the manuscripts was collected prior to the LDRD-LW award by Dr. Meulenberg and Dr. Lee, who were supported by an OBES award at the time. This data was, in part, used by Dr. Meulenberg in his proposal/presentation for the LDRD-LW competition. Moreover, the vast majority of data presented in the three papers was collected at OBES-funded synchrotron facilities which necessitated an acknowledgement to OBES.

Paper 1: R.W. Meulenberg^{*}, J.R.I. Lee^{*}, S.K. McCall, K.M. Hanif, D. Haskel, J.C. Lang, L.J. Terminello, T. van Buuren, "Evidence for Ligand Induced Paramagnetism in CdSe Quantum Dots", *J. Am. Chem. Soc.*, 2009, **131**, 6888-6889 (also featured as a 'Research Highlight' in *Nature*, 2009, **459**, 302-303)

Evidence for Ligand Induced Paramagnetism in CdSe Quantum Dots

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The appearance of magnetism in otherwise non-magnetic materials has recently been reported for a number of nanoscale systems. Coupled with the size-dependent optical and electronic properties of the nanocrystalline materials, this magnetic behavior opens the possibility for an extended range of technological applications. As such, identifying the origin of the magnetism is an extremely important goal, yet this remains the subject of some controversy in the literature. For instance, two previous studies have shown that Au, a 5d⁹ metal, exhibits ferromagnetic behavior in the nanocrystalline form^{1,2} but the authors propose conflicting mechanisms. Meanwhile, a recent observation of magnetization in PbSe quantum dots (QDs) suggests that the magnetism is intrinsic to the QD and not due to a surface effect.³ More recently, induced magnetism has been reported for CdSe QDs⁴⁻⁶ and attributed to a variety of sources that include the existence of dangling bonds,⁴ induction by surface ligands⁵ and even defects in the CdSe particles.⁵ Adding more complexity to these observations is the fact that none of these studies systematically investigate both the size and surface ligand effects and two of these reports⁵ claim that the observed magnetism is due to ferromagnetic ordering. In this communication, we provide conclusive evidence that magnetism in CdSe QDs can be induced via manipulation of the surface chemistry. It is demonstrated that one can enhance the paramagnetic behavior of the CdSe QDs by variation of the endgroup functionality of the passivating layer with no evidence for ferromagnetism.

Magnetic susceptibility measurements were made using a SQUID magnetometer and provide evidence of changes in the magnetic properties of the CdSe QDs when compared to bulk CdSe. Figure 1 displays $\chi(T)$ for 15 Å radius CdSe QD samples passivated with hexadecylamine (HDA) or trioctylphosphine oxide (TOPO) and the expected value for bulk CdSe. The QD samples obey a modified Curie law with $\chi_0 > 0$ and Curie constants, C , strongly dependent on the surface termination $C = 32(1.2) \times 10^{-6} \text{ emu K g}^{-1}$ for TOPO (HDA) surface ligand passivation. These values only consider the total sample mass, and do not separate the contributions due to the surface ligands. This aspect, along with a complete size dependent study, will be addressed in detail in a future manuscript. Atomic emission indicates non-Cd transition metal impurities are <1 ppb, suggesting that chemical bonding induces local paramagnetic moments on the particle surface. Both $\chi(T)$ and $M(H)$ scans indicate there is no ferromagnetic ordering in these samples, so experiments were performed to ensure that we could attribute the

observed paramagnetism to a surface effect. We have performed both x-ray magnetic circular dichroism (XMCD) and x-ray absorption spectroscopy (XAS) to directly probe the Cd electronic structure of the particles. Since we propose the magnetic properties are induced by a chemical bonding effect, XMCD experiments at the Cd L₃-edge (probing 4d states where chemistry is most likely to occur⁹) should yield detailed element specific information about the spin polarization in these materials. As plotted in the Figure 1 inset, CdSe-TOPO QDs ($R = 13 \text{ Å}$) exhibit an XMCD signal at 3542 eV, an energy where vacant Cd d levels are expected to arise.¹⁰ The signal is on the order of $\sim 5 \times 10^{-4}$, which is consistent with a moment of $\sim 0.01 \mu_B/\text{Cd}$. Although this value for the magnetic moment is consistent with both $\chi(T)$ and our $M(H)$ measurements,⁸ it must be noted that the signal is only ~ 2 above the noise, so more experiments would be required for a more conclusive measurement.

When considering the temperature independent part of the magnetic susceptibility, the appearance of positive values is intriguing because bulk CdSe has $\chi = -0.334 \times 10^{-6} \text{ emu g}^{-1}$.⁷ If one considers the diamagnetic contribution from the TOPO and HDA ligands ($\chi = -0.73 \times 10^{-6}$ and $-1.4 \times 10^{-6} \text{ emu g}^{-1}$, respectively), then the overall magnetic susceptibility for the QD materials should be slightly more negative than that of bulk CdSe. Thus, ignoring interaction effects, one would expect that the value of bulk CdSe would be an upper limit on the magnetic susceptibility,

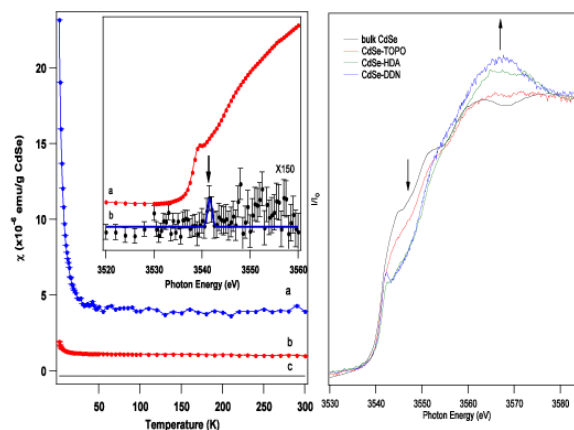


Figure 1. (Left panel) Magnetic susceptibility for $R = 15 \text{ Å}$ CdSe QDs passivated with (a) TOPO, (b) HDA, and (c) bulk CdSe. The inset plots Cd L₃-edge (a) XAS and (b) XMCD measurements for a 13 Å CdSe-TOPO QD. The blue line (inset) is a guide for the eye. (Right panel) Cd L₃-edge XAS spectra of bulk CdSe and $R = 15 \text{ Å}$ CdSe QDs passivated with TOPO, HDA, and DDN.

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which is not experimentally observed. This behavior can be explained by considering the main components of magnetic susceptibility, χ , which can be described as $\chi = \chi_c + \chi_L + \chi_s + \chi_{VV}$ where χ_c is the core-electron diamagnetic contribution, χ_L is the Langevin contribution, χ_s is the surface ligand diamagnetic contribution, and χ_{VV} is the Van-Vleck contribution. While χ_c , χ_L , and χ_s are negative contributors to the magnetic susceptibility, χ_{VV} is a positive value and represents the paramagnetic contribution to the magnetic susceptibility. According to Ref.7, both χ_L and χ_{VV} should vary with particle size as χ_L depends on the bond length, a size dependent value¹¹ and χ_{VV} depends on the matrix elements between the bonding cation orbitals and antibonding anion (or ligand) orbitals, which we propose change with surface termination. What this implies experimentally is that both the lattice contraction and the increasing degree of charge transfer bond between the Cd atoms and the surface ligands should result in a positive χ_{VV} value, although charge transfer is expected to play a more dominant role (see Suppl. Info.). This charge transfer effect can manifest itself in the form of π -backbonding, with the degree of backbonding depending on the ligand-acceptor strength. Following the π -acceptor scale,¹² we expect TOPO > HDA as a π -acceptor and similar trends in the strength of charge transfer. We note that although TOPO is aphosphine oxide, trioctylphosphine impurities in the TOPO passivate some of the CdSe QD surface.¹³ In addition, we would expect that although oxygen is typically thought of as a donor atom, the P=O bond of TOPO contains empty π^* orbitals and should therefore be a good π -acceptor. Therefore, the correlation between the positive χ_{VV} values and the increase in the ligand π -acidity indicates that paramagnetism is arising from the molecular level interactions occurring between Cd atoms and the surface ligands.

One oddity in this observation is that the alkylamines possess no low-lying orbitals and do not provide an obvious means of withdrawing electron density from the d -orbitals of Cd. It is suggested therefore, that the paramagnetic properties of the CdSe-HDA QDs are induced by a chemical impurity in the bulk HDA solvent. Time of flight-secondary ion mass spectrometry (TOF-SIMS) measurements verify that organic impurities are present in bulk HDA and, as a result, present on the surface of the CdSe-HDA QDs. In addition to the anticipated signature for HDA, the TOF-SIMS spectra provide evidence for molecules containing the cyano (-CN) group within the HDA solvent and the CdSe-HDA QD samples. The presence of the cyano functionality is extremely significant because, in contrast to the amine group of HDA, -CN is capable of accepting Cd $4d$ electron density via back-donation into the π^* -orbitals of the CN triple bond. Indeed, when the ligand, dodecanitrile (DDN), was intentionally ligand exchanged onto the CdSe QD surface, a modest increase in the Curie constant ($C = 3.8 \times 10^{-6}$ emu K g⁻¹) was observed via magnetic susceptibility (Figure S2). This result implies that we can "switch" the magnetic behavior "on and off" on one particle simply by changing the ligand molecule on the same particle. Therefore, as the TOPO ligand can also participate in π -backbonding, backdonation between the Cd and -XL (where X is endgroup functionality and L is the ligand) is proposed as the mechanism for enhancement of the vacant d -DOS and the origin of paramagnetic properties in the CdSe QDs.

Although the (T) and XMCD data provide strong evidence of a surface termination driven dependence of the magnetic susceptibility, one must address the contribution that dangling bonds may play in the magnetic properties of the CdSe QDs. As shown in the dilute magnetic semiconductor literature and in radiation damage studies of normally nonmagnetic systems,¹⁵ defects can play a role on determining the magnetic properties of

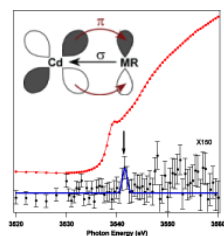
these systems. As our QDs are of the highest quality, however, we do not expect any defect induced magnetism to be present. We have previously shown that Cd L_{3-} -edge XAS is an excellent tool to probe the s and sp hybridized DOS.¹⁶ Since the XAS experiments enable investigation of sp hybridized states, the measurements can indirectly probe the relative amount of empty p -like states in the CdSe QDs that are related to dangling bonds as predicted by theory.¹⁰ The right panel of figure 1 plots the Cd L_{3-} -edge XAS spectra for 15 Å radius CdSe QDs passivated with different surface ligands alongside the bulk CdSe spectrum. In the energy region between 3540-3550 eV, a large reduction (15%) in XAS intensity (decrease in empty states) is seen as the ligand changes from TOPO to HDA which is consistent with the relative increase in passivation by HDA.^{9c} Even so, the associated reduction in the number of dangling bonds cannot account for the nearly order of magnitude increase in the Curie constant as suggested by Neeleshwar et al.⁴ In addition, the dangling bond concentrations derived in Ref.4 do not make physical sense; a concentration of 2000 ppm for 14 Å radius CdSe QDs gravely underestimates the number of dangling bonds considering the wealth of literature on this subject.¹ By ruling out dangling bond contributions the contrasting behavior of the CdSe-HDA, CdSe-TOPO, and CdSe-DDN systems indicates that the paramagnetic properties of the CdSe QDs are dependent upon their interaction with the organic ligand molecules.

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SUPPORTING INFORMATION AVAILABLE Synthesis, ligand exchange and characterization (TEM, UV-Vis), experimental details magnetization measurements, charge transfer model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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We report evidence that paramagnetism in CdSe QDs can be induced via manipulation of the surface chemistry. Using SQUID magnetometry and x-ray absorption spectroscopy, we demonstrate that the paramagnetic behavior of the CdSe QDs can be varied by changing the ligand endgroup functionality of the passivating layer. Contrary to previous reports, no evidence for ferromagnetism was observed. The results suggest that the paramagnetism is induced via π -backbonding between Cd 4d orbitals and ligands with empty π^* -orbitals.

Paper 2: R.W. Meulenber^{*,†,§}, J.R.I. Lee^{*,†}, A. Wolcott, J.Z. Zhang, L.J. Terminello, T. van Buuren, "Determination of the Exciton Binding Energy in CdSe Quantum Dots", *ACS Nano*, 2009, **3**, 325-330

Determination of the Exciton Binding Energy in CdSe Quantum Dots

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Abstract

The exciton binding energy (EBE) in CdSe quantum dots (QDs) has been determined using x-ray spectroscopy. Using x-ray absorption and photoemission spectroscopy, the conduction band (CB) and valence band (VB) edge shifts as a function of particle size have been determined and combined to obtain the true band gap of the QDs (i.e. without and exciton). These values can be compared to the excitonic gap obtained using optical spectroscopy to determine the EBE. The experimental EBE results are compared with theoretical calculations on the EBE and show excellent agreement.

In the field of colloidal quantum dot (QD) materials, the effects of quantum confinement (QC) as a function of QD particle size represent some of the most widely studied QD phenomena. Included in these QC effects is the increase in exciton energy as the particle size is reduced below the

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bulk Bohr exciton radius giving rise to unique optical properties that are highly tunable with particle size.¹ In CdSe QD materials, tunable optical properties are exhibited by particles in the 100 Å diameter and below range, because the bulk Bohr exciton radius for CdSe is 56 Å.² Recently, there has been some controversy regarding the scaling of the exciton binding energy (EBE) with particle size. Early models, such as those based on the particle-in-a-box (PIAB),³ were used to predict that the EBE scales as the inverse of the particle radius, R^{-1} , which simply represents the Coulomb interaction between the electron and hole. More sophisticated theories, however, have predicted a deviation in the scaling of the EBE with particle size. For instance, Franceschetti and Zunger⁴ have used the empirical pseudopotential method (EPM) to predict that the EBE actually has a sublinear scaling factor $R^{-0.86}$, for CdSe QDs. The apparent failure of the PIAB method is related to a few factors that include the use of a size-independent dielectric constant and crude boundary conditions for the wavefunctions (i.e. an infinite potential well at QD surface) in the model. Despite the rich literature on the theoretical description of the EBE for CdSe QDs, there has been no experimental investigation of the EBE. Irrespective of the theoretical methods used to calculate the EBE in CdSe,^{4,5} it is evident that the size induced increase in the EBE is much larger than the thermal energy making a simple temperature dependent optical absorption study incapable of deriving this quantity. In this letter, we report on the determination of the EBE for CdSe QDs. We find that the scaling of the EBE with particle size is sublinear and is in close agreement with the values predicted using EPM theory⁴.

One possible explanation for the predominance of theoretical studies of the EBE can be attributed to the inherent difficulties associated with an experimental determination. Ultra-violet/visible absorption spectroscopy is a very common analytical tool used in the characterization of CdSe QDs as the lowest energy absorption feature (the first exciton) can yield information on the QD size, crystallinity, and size dispersion.⁶ In addition, multiple exciton states can be resolved at higher energy for high quality QDs.⁷ The overriding problem with these studies, however, is that the excitonic states dominate the optical properties and the true electronic bandgap (BG) remains unresolved (see Figure 4B for a description of the difference between the optical and electronic

band gap). The most elementary description of the electronic BG exists as the energy difference between the highest occupied states (valence band, VB) and the lowest unoccupied states (conduction band, CB). This value is fundamentally different than the excitonic states, which can occur anywhere from a few to hundreds of millielectron volts below the CB minimum (15 meV for CdSe versus 1 eV for LiF).⁸ A means of obtaining the electronic BG independent of the excitonic energy is of utmost importance in determining the EBE.

X-ray spectroscopies provide ideal methods with which to elucidate the absolute electronic BG energy of CdSe QDs. We have previously shown that the unoccupied states (CB states), can be independently resolved with elemental specificity using X-ray absorption spectroscopy (XAS).⁹ For CdSe QDs, the CB minimum shifts to higher energy with decreasing particle size in accordance with quantum confinement theories. In this manuscript, the filled states (VB states) are directly probed using valence band photoemission spectroscopy (VBPES). With VBPES, measurement of the ionization energies and energy profile of photoelectrons emitted from the VB yields the occupied VB DOS and enables an assignment of the energy of the VB maximum. One can, therefore, obtain the electronic BG by combining the energies of the VB maximum and CB minimum determined experimentally using VBPES and XAS. Subsequent comparison of the electronic BG with the excitonic gap obtained from optical absorption measurements will yield the EBE.

Results and Discussion

Figure 1 plots valence band photoemission (VBPES) spectra of different sized CdSe QDs and the corresponding bulk spectrum all excited at 90 eV. The bulk CdSe VBPES, shown in Figure Figure 1c, maps out the occupied DOS which consist of Se 4p orbitals at the top of the VB with the Cd 4d orbitals 11 eV below the VB maximum. Although soft x-ray fluorescence (SXF) spectroscopy can be used to provide information on the VB DOS, for edges like the Se₃L edge, the main decay channels occur through the core levels, obscuring any valence band features. SXF measurements were also attempted at the Se 4s edge as the Heske group has observed the upper valence band

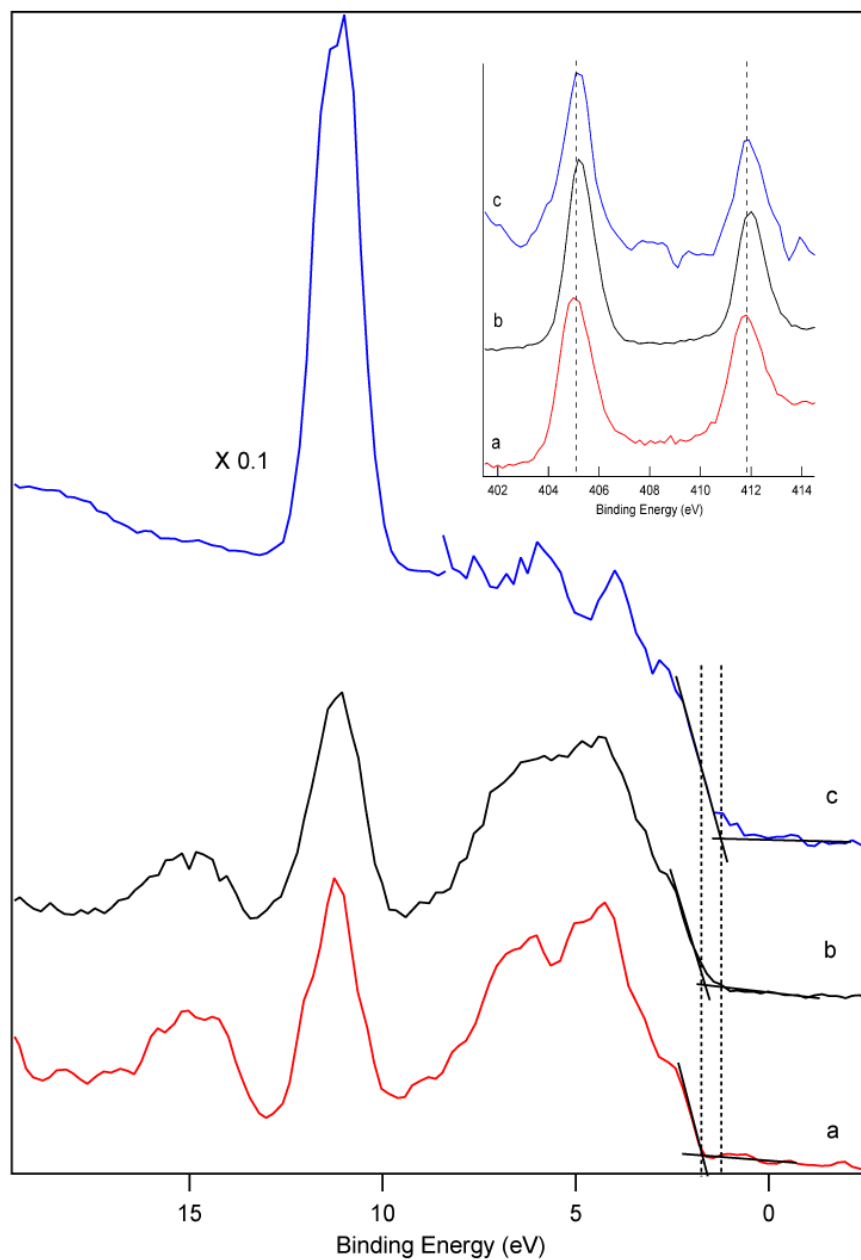


Figure 1: Valence band photoemission spectra of (a) 15 and (b) 19 Å radius CdSe QDs and (c) bulk CdSe(0001) wafer. Inset: Cd 3d_{5/2} and 3d_{3/2} core level PES spectra of the same size samples.

levels in CdS materials using S L_3 XES.^{10,11} In our experiments, however, we were only able to observe the core levels and not the valence band levels, with our measurements resembling previous work performed on spinels using Se M_3 SXF.¹²

The observed integrated intensity ratios between the Cd and Se 4p (VB), I_{4d}^{Cd}/I_{VB}^{Se} , is $\sim 20:1$, which is consistent with both the atomic photoionization cross sections at 90°¹³ and previous VB-PES measurements on bulk CdSe.^{14,15} To determine this ratio, the respective peaks were fit to Gaussian lineshapes. The Se component of the VB is modelled as a symmetric Gaussian lineshape with the "notch" considered to be the "peak" of the spectrum. Although the QD VB-PES show similar features, an additional contribution to the DOS is observed between 5-7 eV that is attributed to carbon related features (capping molecules). Gentle heating of the NC samples, a practice known to remove some of the organic surfactant, leads to a decrease in the spectral intensity between 5-7 eV, which supports the assignment of these features to contributions from carbonaceous materials. We note that even high temperatures did not result in the complete reduction of the carbon features, thereby demonstrating that some amount of pyridine capping agent is chemisorbed to the particle at all times.¹⁶ In addition, the introduction of other capping groups with less carbon than pyridine, i.e. TGA (spectrum not shown), does not yield a reduction in the DOS features between 5-7 eV. We believe this arises from the fact that the sulfur moiety of the TGA is more tightly bound to the CdSe particle than the nitrogen atom of the pyridine. This, in turn, results in a larger carbon "signal" in the VB-PES and helps us to assign the features to carbon.

The inability to remove all carbon contributions from the VB-PES spectra induces some level of error into determining the absolute energy of the VB edge for a CdSe QD. Nonetheless, analysis of the intensity ratios between the Cd and Se 4p indicate that the VB edge can be described in terms of the CdSe QDs and not of the carbon features on the surface of the particle. The obtained ratio, I_{4d}^{Cd}/I_{VB}^{Se} , for the QDs is $\sim 5:1$, which is a factor off our lower than observed in the bulk CdSe sample. The lower ratio can be explained by considering that the CdSe surface contains an excess of Se atoms. A recent study¹⁷ has proposed that CdSe QD surfaces have nearly a 50% excess of Se which could explain the differences in the ratio for our samples. As this experiment is based

upon the detection of 90 eV kinetic energy electrons that have a mean free path of up to 10 nm, we are preferentially probing the QD surfaces and should be extremely sensitive to local changes in stoichiometry.

Figure 2 plots the observed VB shifts for CdSe QD samples with two different surface terminations, pyridine and TGA. The values for both the valence and conduction bands shifts are listed in Table 1. For energy calibration purposes, all the spectra were referenced to Cd 3d core level

Table 1: Experimental valence and conduction band shifts relative to the bulk values. The CdSe radius is measured in Å, ΔE_{VB} is the difference between the QD and bulk VB edge and ΔE_{CB} is the difference between the QD and bulk CB edge (both in eV)

CdSe particle radius	ΔE_{VB}	ΔE_{CB}
19	0.16	0.65
15	0.66	0.65
14	0.77	0.72
6.25	2.04	1.20

PES spectra that were, in turn, calibrated versus Au 4f core level spectra from the underlying substrate. The Au offers an optimal means of calibration because the energy of the Au orbitals are well characterized and the Fermi levels of the QDs and the substrate are aligned¹⁸ Interestingly, and in contrast to previous reports,^{19,20} we do not observe a shift in the Cd 3d core levels. This result, although somewhat surprising, is reproducible over long time scans and multiple sample preparations. Moreover, our results are similar to early studies on CdSe QDs where shifts of less than 0.1 eV (i.e. less than the experimental resolution) were observed.²¹ We have great confidence in the validity of the results presented in this letter for several reasons: (a) Comparison of the Cd 4d levels with respect to the Se 4p dominated VBM (Figure Figure 1) indicates that we are truly studying the QDs. In Ref. 19 and 20, the authors fail to discuss the Cd 4d levels in their analysis of the CdSe VB. Examination of the intensity profiles of the Cd 4d levels and the VBM is essential to ensure that one is truly studying the VB of the CdSe material, and not spurious carbon or impurities which may have a stronger VB photoemission cross section. (b) Plots of both the Cd 5_{3/2} and 3d_{3/2} provide no evidence for sample oxidation (inset of Figure 1). (c) Multiple spectra recorded on both identical and distinct regions of each sample show little variation in the CdSe peak position ($2\sigma < 0.05$ eV). This indicates that sample charging plays no role in our experiments. (d) Our

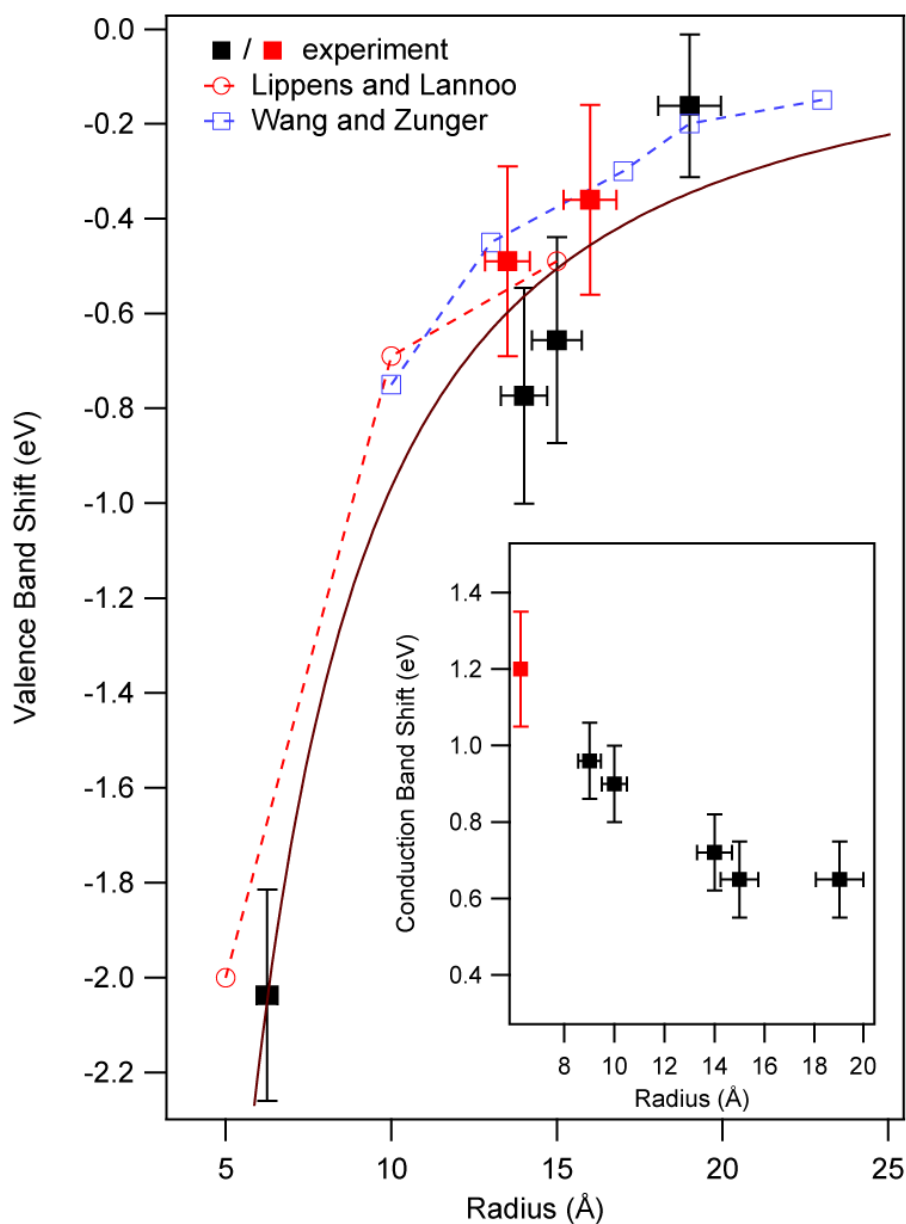


Figure 2: Size dependent values for CdSe QD valence band states. The and represents the pyridine and TGA data points, respectively, while the (Ref. 24) and (Ref. 25) represent theoretical values. The lines for the theoretical points are guides for the eye, while the lines through the experimental points represents a least squares fitting of the data. Inset: Size dependent values for CdSe-TOPO QD conduction band shifts (Ref. 9).

reference spectra were recorded for a clean CdSe(0001) wafer. Using a well ordered crystal allows us to directly compare our results to published data,^{14,15,22,23} and to perform gentle heating of the wafer to drive offphysisorbed organic contaminants. We attempted similar experiments on a CdSe powder and were unable to obtain a clean CdSe VB spectrum. In Refs. 19 and 20, the authors use CdSe powder as a reference rather than a CdSe crystal. Each of these factors provides strong support for the accuracy of our measurements and the associated discussion presented in this letter. Furthermore, they allow us to conclude that the shifts observed in our data can be described in terms of quantum confinement induced changes in the VBM, as opposed to core level / Fermi level shifting.

For the purposes of comparison, theoretical values^{24,25} for the VB shifts have been plotted alongside the experimental data. There is excellent agreement between experiment and theory, with the majority of the experimental values residing within experimental error of the theoretical values. In fact, the agreement between experiment and theory is far superior to the equivalent comparison reported in our XAS characterization of the CBM.⁹ In addition, we observe similar VB edge shifts for different surface terminations suggesting that the capping molecules does not affect the VB edge energy to any significant degree. The lack of surface sensitivity on the edge shifts is consistent with optical measurements.²⁶ For comparisons sake, the scaling laws associated with the VB and CB levels are,

$$E_{VB} = E_{VB}^{bulk} - \frac{38}{R^{1.6}} \quad (1)$$

$$E_{CB} = E_{CB}^{bulk} + \frac{4}{R^{0.6}} \quad (2)$$

where the numerator for the second term for both equations are in units of eV Å. For a more complete picture of the CdSe QD electronic structure, the experimental band gaps as a function of particle radius are plotted in Figure 3. The photoemission PE band gap is defined as the addition of the CB shift and VB shift to the bulk CdSe value,

$$E_{BG}^{PE} = E_{CB} + E_{VB} + E_{bulk}^{CdSe} \quad (3)$$

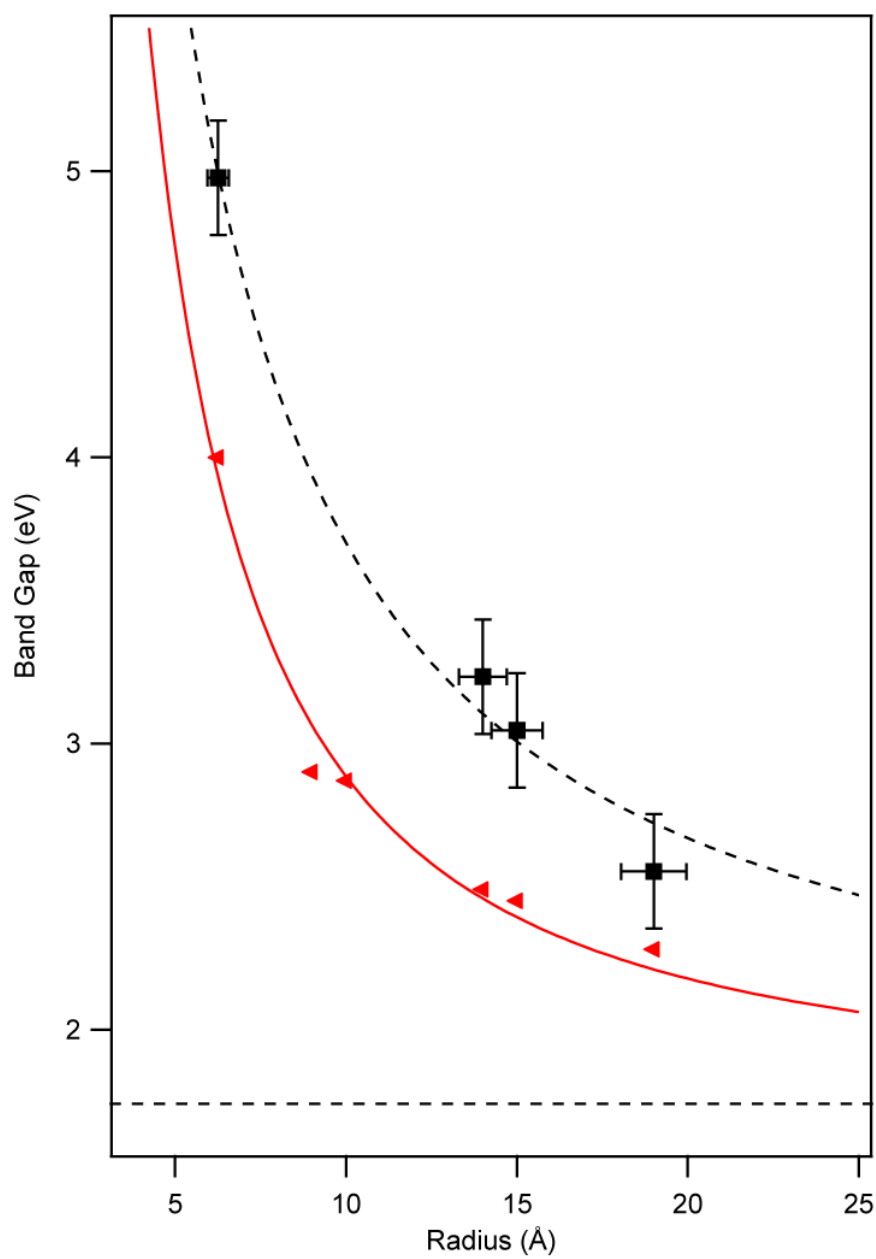


Figure 3: Band gap of CdSe QDs as a function of particle radius. The \blacksquare represents the CdSe QD photoemission band gaps, the \blacktriangle represents the CdSe optical absorption excitonic gaps.

, where $E_{\text{bulk}}^{\text{CdSe}} = 1.74$ eV (at 300 K).⁸ The PE gap () is plotted alongside the optical absorption (OA) excitonic gap () for purposes of direct comparison. Both the PE and OA gaps show a similar scaling with size, $R^{-0.6}$ and $R^{-0.7}$, respectively.

Although the scaling for the two measurements are similar, an obvious offset is present between the two data sets. If one takes the difference between the two data sets and plots them as a function of size (Figure 4), it is evident that the difference increases with decreasing particle size. This difference is the EBE and the conceptual derivation of this value is illustrated in Figure 4B. Put simply, the EBE is the difference between the electronic band gap (from PES) and the excitonic gap (from optical absorption). Remarkably, the overlap between our experiment and theory is excellent. The scaling law associated with the experimental EBE can be written as $EBE \propto 1/R^n$, where $n = 0.72$. Franceschetti and Zunger⁴ have shown theoretically that $n = 0.86$ for CdSe QDs using the empirical pseudopotential method (EPM). Both experiment and EPM theory predict that the EBE scales sublinearly with particle size, in contrast to the PIAB model which predict the EBE scales inversely proportional with particle size (Coulomb energy).

One factor that is neglected in this discussion is the contribution of the exciton binding energy (CEBE). It has been previously reported that the size dependent increase in the CEBE in CdS QDs led to strong features in the λ_3 absorption edge and made straightforward analysis of the edge onset difficult.²⁷ As a consequence, an important question arises for CdSe QDs: must the CEBE be considered in this analysis? To answer this question, one must consider the strength of the CEBE in the bulk material and how a reduction in particle size may affect the value. Following Carson et al,²⁸ the CEBE can be described by,

$$E_{\text{CEBE}} = R_H \left(\frac{\mu}{\epsilon^2} \right) \quad (4)$$

, where R_H is an atomic Rydberg constant, μ is the reduced mass, and ϵ is the dielectric constant.

Using Eq. 2, the values of E_{CEBE} are ? 10 and 100 meV for bulk CdSe and CdS, respectively.

Without knowing the exact effect that quantum confinement has on the CEBE, we need to make an

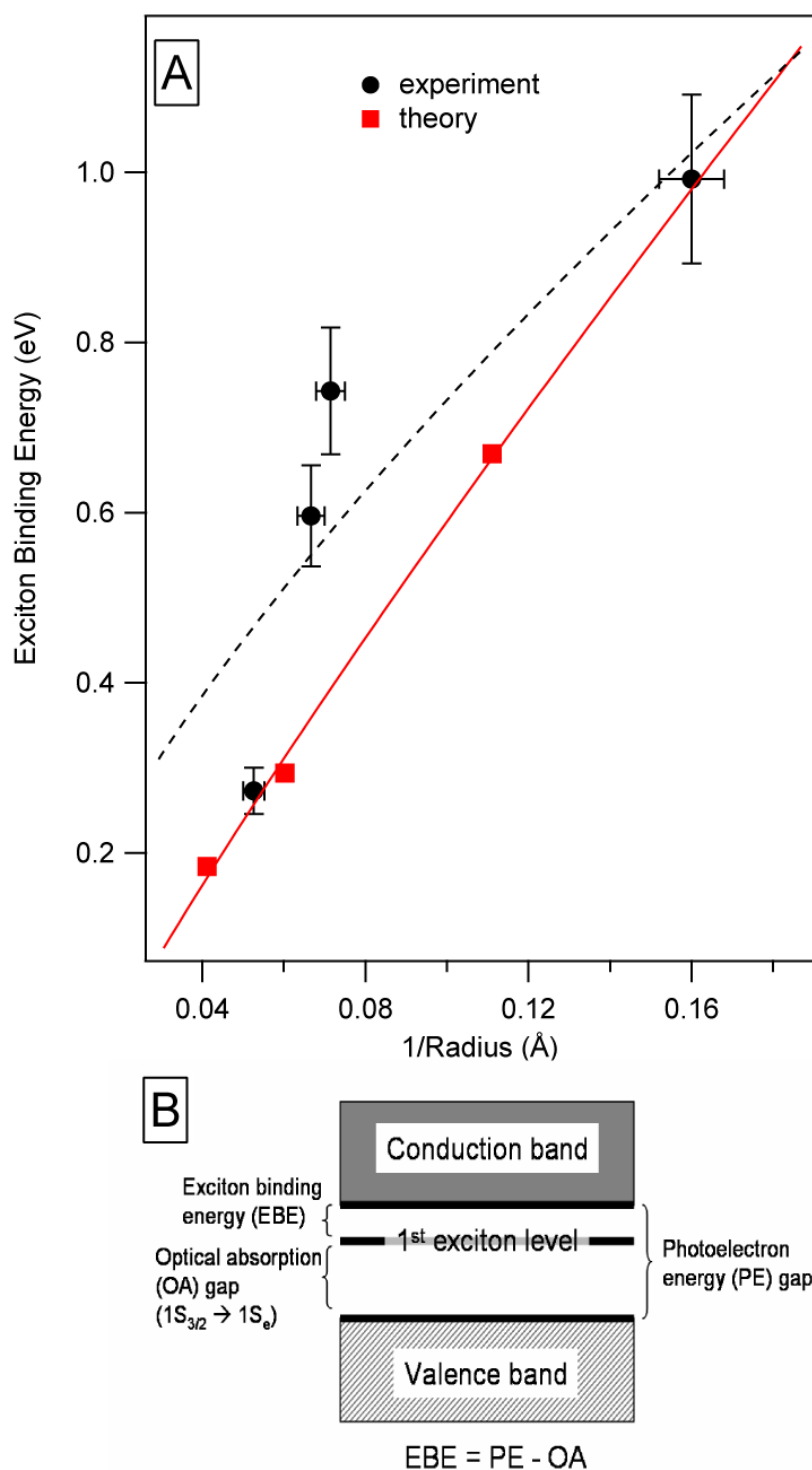


Figure 4: (A) Exciton binding energy of CdSe QDs as a function of particle radius. The represents the CdSe-TOPO QD experimental exciton binding energy while the represents the theoretical values (Ref. 4). (B) Illustration of energy bands depicting the definition of the exciton binding energy, optical absorption gap, and photoelectron band gap.

assumption on the scaling of the CEBE with particle size. If we consider that the CEBE increases by an order of magnitude (i.e. a large increase) at small particle sizes, we can estimate that the CEBE increases to 100 and 1000 meV for CdSe and CdS, respectively. When we consider that the values that we obtained for the EBE were on the order of 1 eV for small particles of CdSe, the exclusion of the CEBE provides an upper range of the error of this value (10%). In the case of CdS QDs, the size induced increase of the CEBE may rival the value of the EBE and it is understandable why the CEBE could not be ignored in Ref. 27. In the case of CdSe, however, the CEBE is on the order of typical experimental error and can be neglected in this current analysis.

Conclusions

In conclusion, we have obtained the EBE of CdSe QDs using x-ray spectroscopy. The EBE is size dependent and can reach values of nearly 1 eV at the smallest particle sizes studied. The experimental EBE values were compared to those obtained by EPM theory and a strong agreement is observed. These results illustrate that x-ray spectroscopy is a valuable tool to observe new physics that it is not possible to address with more conventional methods.

Acknowledgements

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Methods

Synthesis of CdSe quantum dots

CdSe QDs were produced by previously reported methods using precursors of cadmium oxide (CdO), dimethylcadmium ($\text{Cd}(\text{CH}_3)_2$), tetradecylphosphonic acid (TDPA), trioctylphosphine oxide (TOPO) and hexadecylamine(HDA).^{29,30} The QDs were then dispersed in toluene and then precipitated with methanol several times to remove unreacted precursors and residual capping ligands. Final dispersions of clean CdSe QDs were in hexane. In general, high quality core level PES data was obtained for QDs with this surface termination, but VB PES data of comparable quality was difficult to obtain.

Ligand exchange of CdSe quantum dots

To mitigate the problem observed with TDPA/TOPO/HDA coated QDs, we then studied QDs overcoated with pyridine or thioglycolic acid (TGA), which were prepared from the original CdSe samples via established ligand exchange techniques.²⁶ The ligand exchange was performed for two reasons: (a) to aid in reducing carbon related features in the VB which obscure the valence band edge features of the QDs and (b) to help reduce charging during the PES measurements. The TDPA/TOPO/HDA combination contains many carbon atoms (i.e. TOPO possesses 24 carbon atoms), while pyridine and TGA contain 5 and 2 carbon atoms, respectively. Hence, the ligand exchange results in a substantial reduction in carbon content per capping molecule. The pyridine ligand is also labile in vacuum and, since the pressure in our PES chamber is 5×10^{-9} Torr, we can anticipate that some of the pyridine will desorb, leading to a further reduction in the carbon (organic) features in the VB. Long alkyl chains, a feature of both TOPO and HDA, are insulating and can limit charge transfer from the QD to a surface, which can lead to sample charging.³¹ The use of a short aromatic chain, like pyridine, facilitates charge transfer and reduces any charging effects. The general features in the PES spectra of the three different sample sets are extremely similar, with the main differences apparent in the VB region.

Valence band and core level photoemission measurements of CdSe quantum dots

Valence band and core level PES measurements were performed at beamline 8-2 at the Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center. The CdSe QDs samples were deposited onto Si(111) wafers from hexane. To ensure integrity of the samples, we employed a few protocols. First, different samples were measured from different synthetic preparations. Second, spectra were recorded before and after exposure to the intense x-ray beam to look for any beam damage or charging effects. Third, a consistent method to preparing our films was employed. A small amount (1mg) of QD samples was dissolved in 1 mL of solvent. With an Eppendorf, amounts on the order of 10 μ L were added dropwise to the Si substrate and repeated to ensure a thick enough film would be formed (to eliminate contributions from Si valence band features). QD samples were also prepared in an identical manner on Au coated Si(111) for the purposes of core level calibration studies using PES. The photoelectrons were detected with a cylindrical mirror analyzer with a pass energy of 25 eV which provides an experimental energy resolution of 0.2 eV. All the VB-PES spectra were recorded at an excitation energy, E_{ex} , of 90 eV, while the core level PES spectra were collected using $E_{ex} = 530$ eV unless otherwise noted.

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Experimental Observation of Quantum Confinement in the Conduction Band of CdSe Quantum Dots

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Abstract

X-ray absorption spectroscopy (XAS) has been used to characterize the evolution in the conduction band (CB) density of states of CdSe quantum dots (QDs) as a function of particle size. We have unambiguously witnessed the CdSe QD CB minimum (CBM) shift to higher energy with decreasing particle size, consistent with quantum confinement effects, and have directly compared our results with recent theoretical calculations. At the smallest particle size, evidence for a pinning of the CBM is presented. Our observations can be explained by considering a size dependent change in the angular momentum resolved states at the CBM.

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Semiconductor quantum dots (QDs) are known to exhibit size-dependent optical and electronic properties and, as a consequence, offer considerable potential for a diverse range of technological applications. While changes in the optical properties with QD size can be explained in terms of quantum confinement effects, further study of many nanocrystalline semiconductors is essential if they are to be successfully integrated into new or existing devices. In particular, characterization of the electronic structure remains of fundamental importance in developing a comprehensive understanding of their optical and electronic behavior and, therefore, optimizing functional performance. In this manuscript, we report the first experimental study of the evolution in the conduction band density of states (CBDOS) of a binary semiconductor QD as a function of particle size. X-ray absorption spectroscopy measurements of the size-dependent CBDOS structure of CdSe QDs are used to explain conflicting results obtained from theoretical calculations based upon quantum confinement effects.

In contrast to many binary semiconductor quantum dots, CdSe QDs are readily synthesized with narrow size distributions and possess excellent photochemical stability when passivated properly. [1, 2] In addition, they demonstrate size dependent photoluminescence that encompasses the visible region of the electromagnetic spectrum. [3] Hence, CdSe represents an archetypal system for numerous QD applications (including uses in biomedical imaging and laser diodes) and an ideal model for the study of quantum confinement effects. Although extensive research has been devoted to characterization of the electronic structure in CdSe QDs, [4, 5] the size-dependent evolution of the valence band (VB) and CBDOS remain unresolved from one another via experimental study. It has been demonstrated that theoretical calculations provide a means for the deconvolution and isolated study of the VB and CB. [6–11] Nonetheless, the results reported for CdSe exhibit strong model dependence, which is illustrated by predicted scaling laws ranging between $E_c \propto R^{-0.8}$ [11] and R^{-2} [9] for size-dependent energy shifts in the bottom of the CBDOS. As such, identification of the most representative theory is paramount.

Several experimental techniques have been used to address the development of the band gap in nanocrystalline CdSe [3, 4, 12, 13] (particularly UV-Visible absorption spectroscopy because it also provides a diagnostic of QD particle size and size dispersion), but the band gap represents only the convolution of the VB and CB and does not allow for an independent treatment of these edges. The application of alternative methods is essential, therefore,

for successful mapping of the electronic structure in CdSe QDs. In previous publications, we have shown that X-ray absorption spectroscopy (XAS) offers the ideal technique with which to probe quantum confinement induced shifts in the lowest unoccupied states (CB) of nanocrystalline materials. [14–17] In this manuscript, we have additionally shown that XAS can be a powerful tool to elucidate the angular momentum resolved quantum shifts as only $\Delta l = \pm 1$ transitions are allowed. Due to this angular momentum specificity, selection of the appropriate absorption edge allows one to focus upon the bottom of the CB. The projected DOS obtained from theory demonstrates that the bottom of the CB is comprised of Cd 5s states (see Figure 1A). Hence, the Cd L_3 edge should be ideal for probing any size dependent effects in this region because transitions between the p initial state and unoccupied s states are dipole allowed. If the bottom of the CdSe CB moves by some energy, ΔE_c , then the L_3 absorption edge should shift by a corresponding amount representing the quantum confinement induced shift in the CB. In principle, the Cd M_2 - and M_3 -edges, which are composed of a p initial state, could also be used to probe the bottom of the CB. The M -edges, however, suffer from weak signals and a large background which limits the usefulness of using these edges for quantitative information.

CdSe quantum dots (QD) with a mean radius ranging from 9-19 Å and coated with the ligand trioctylphosphine oxide (TOPO) were synthesized using a known method. [1] QD size and size dispersion were derived using UV-Visible absorption spectroscopy. [4] Due to the difficulties in producing very small colloidal QDs, a cluster sample of the form $Cd_{10}Se_4(SC_6H_5)_{16}^{4-}$ (Cd_{10}) was prepared using an established technique. [18] This allowed the investigation of very small particle sizes without being limited by colloidal chemistry techniques. It should be noted that the Cd_{10} cluster has a radius of 7 Å [19] and is not coated with TOPO but with thiophenol. While the change in surface structure could have an impact on these experiments, we defer to previous measurements on the electronic structure of CdSe QD while changing surface chemistry which show very small changes in the band edges with surface termination. [3] For the XAS measurements, the QDs were deposited from toluene onto a Si(111) wafer and the solvent was allowed to slowly evaporate. Multiple depositions were performed to ensure a sufficiently thick CdSe film was obtained. XAS experiments were performed on the bend magnet beamline 9.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The measurements were taken in both total electron and total photon yield without any noticeable differences between the

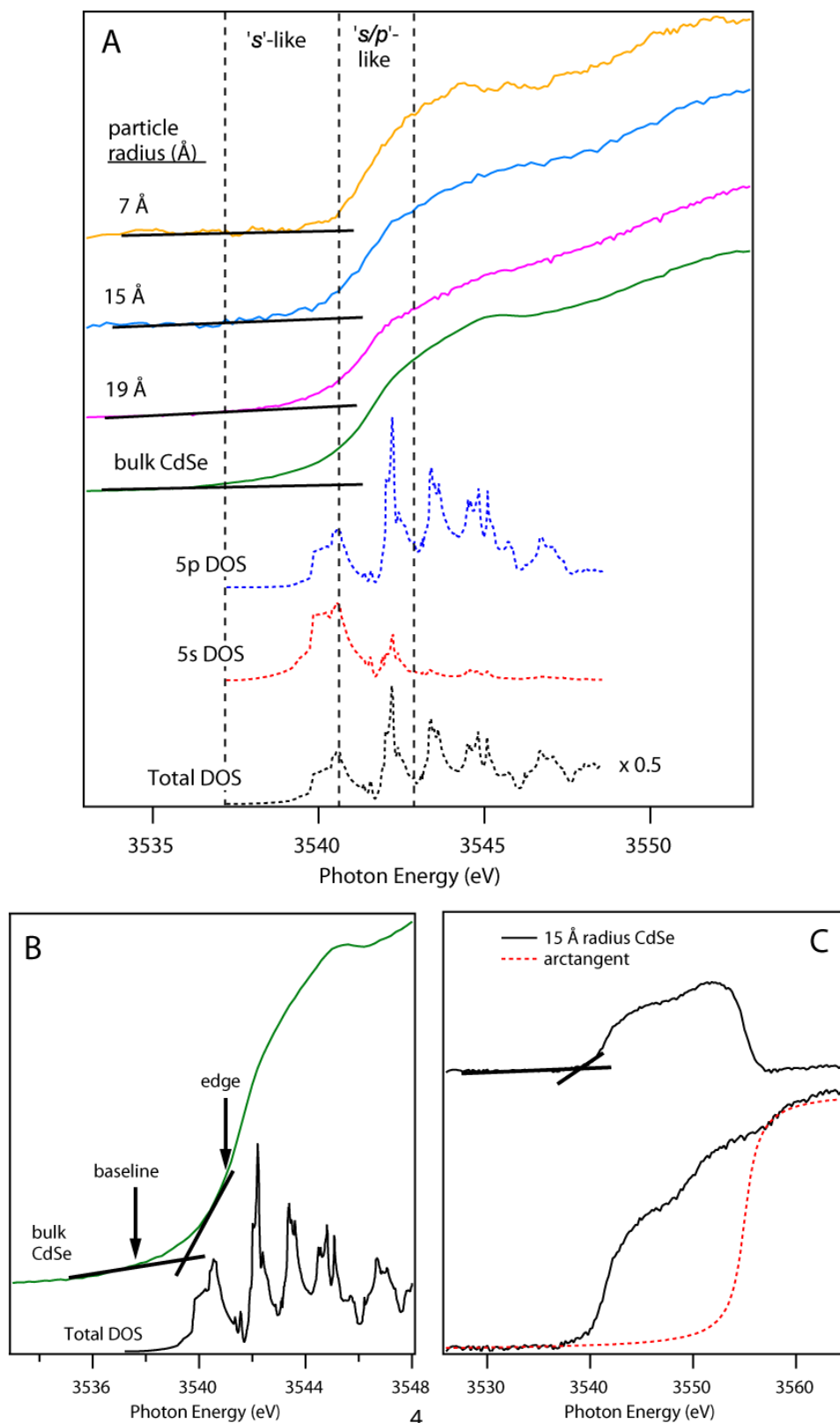


FIG. 1: (A) Experimental Cd L_3 -edge XAS spectra (top four traces) and calculated conduction band (CB) density of states (DOS) for bulk CdSe (bottom three traces) (B) Extrapolation method to derive CB shifts as described in the text. The total DOS are plotted to define the baseline of the

two detection methods. The current from a gold grid, I_0 , was used to normalize the XAS spectra. Although the experimental resolution in these experiments was ~ 0.2 eV with lifetime broadening of ~ 1.0 eV, the accuracy in measurement of the absorption onset energy is considerably better.

Figure 1A plots selected XAS spectra at the Cd L_3 edge for CdSe QDs of different sizes and the corresponding bulk spectrum. For comparison with the experimental CBDOS features, we show the calculated CBDOS for bulk CdSe as a dotted line in Figure 1. The calculated projected CBDOS were obtained using a full-potential linear muffin-tin orbital method. [20–22] The angular-momentum-resolved projected CBDOS were generated on the basis of a Mulliken decomposition and by projecting out against the atom-centered numerical basis functions obtained from the self-consistent calculations. [22–24]

The bulk CdSe L_3 -edge spectrum shows a sharp absorption onset with a distinct foot (Fig. 1A) and additional absorption features ca. 4, 7, and 14 eV above the onset. A noticeable difference in the spectral features between bulk CdSe and the QD samples is a reduction of intensity in the foot of the absorption onset. The calculated CBDOS indicate that the foot in the absorption spectrum is due only to Cd 5s states and composes the CB minimum. Therefore, it is necessary to look at this region of the spectrum in order to identify any shifts in the bottom of the CB that may arise from quantum confinement effects. The presence of significant DOS features near the baseline, however, causes some difficulty in obtaining an absolute measure of the absorption onset. The energy of the absorption onset is obtained by extrapolation of the linear region of the baseline and the linear region of the absorption edge above the threshold and identifying the point at which they intersect. A specific protocol was followed to determine where the extrapolated lines are drawn on the spectrum to warrant self-consistent results (and error). The baseline is extrapolated from the linear component of the pre-edge region and is defined to delineate from the experimental data at the energy for which the calculated CBDOS is non-zero. In other words, the baseline of the experimental spectrum ends at the point where DOS features begin and is $\sim 2\sigma$ above baseline noise. Allowing the DOS features to be defined by points $\sim 2\sigma$ about baseline noise establishes a lower limit on the experimental error in our measurements (~ 0.15 eV). The line on the absorption edge begins at the midway-value between the baseline and step edge and from this point, a tangent is drawn to the edge (see Figure 1B). Using this protocol, values of the extrapolation onset can be obtained with minimal contribution from biased

error. A second and alternative protocol was introduced which sharpens the DOS features present near the baseline. An arctangent function (Figure 1C) was subtracted from the experimental data which allows a more straightforward analysis of the absorption edge. [25] The arctangent function represents transitions between the 2p initial state \rightarrow continuum/free electron states. The values obtained from both data analysis protocols are comparable and indicate that the shifts reported in this letter represent an accurate measure of the evolution of the CB minimum with particle size.

A comparison of the results from the two methods is provided by Figure 2 which displays the CB shifts for the series of CdSe QD samples studied in this letter. For the purposes of direct comparison reported theoretical values [11, 26] have been plotted alongside the data. The reduction of the DOS features in the absorption onset in the QD samples with respect to the bulk CdSe sample is most likely due to quantum confinement induced shifts in the bottom of the CB edge. As seen from Figure 2, the L_3 -edges of the QD samples are shifted to higher energies relative to bulk CdSe. For example, shifts of 0.65 eV to 1.2 eV are observed for the 19 and 7 Å radius CdSe QD samples respectively, which are consistent with the quantum confinement model. The agreement between experiment and both theories is close, but better agreement is seen with the charge patching (CP) theory [11] at larger particle sizes than with the tight-binding (TB) theory [26]. The CP method, which uses the charge density rather than the local potentials to generate the electronic structure, better represents the experimental system for three reasons: (1) The CP theory is a first-principles theory based on the local density approximation (LDA). In the CP approach, the electronic structure is calculated for a small system (i.e. 10-100 atoms) using LDA. The charge density is then generated for the small system and "patched" (added) together in order to produce the charge densities for larger systems. The charge density is then generated for the small system and multiplied in order to produce the charge densities for larger systems. It has been shown that the CP method, when compared to LDA, is accurate on the order of 50 meV error [27] which is smaller than the experimental error. (2) Within the TB theory, a basis set of sp^3s^2 was used, which indicates that the calculated conduction band states are composed of mainly s states with some p state contribution. Although it is believed that shifts will occur from s related states, this basis set gives a relatively crude description of the conduction band. (3) The CP theory includes a hydrogenlike passivation. Although not ideal, it provides a semi-realistic model of the surface.

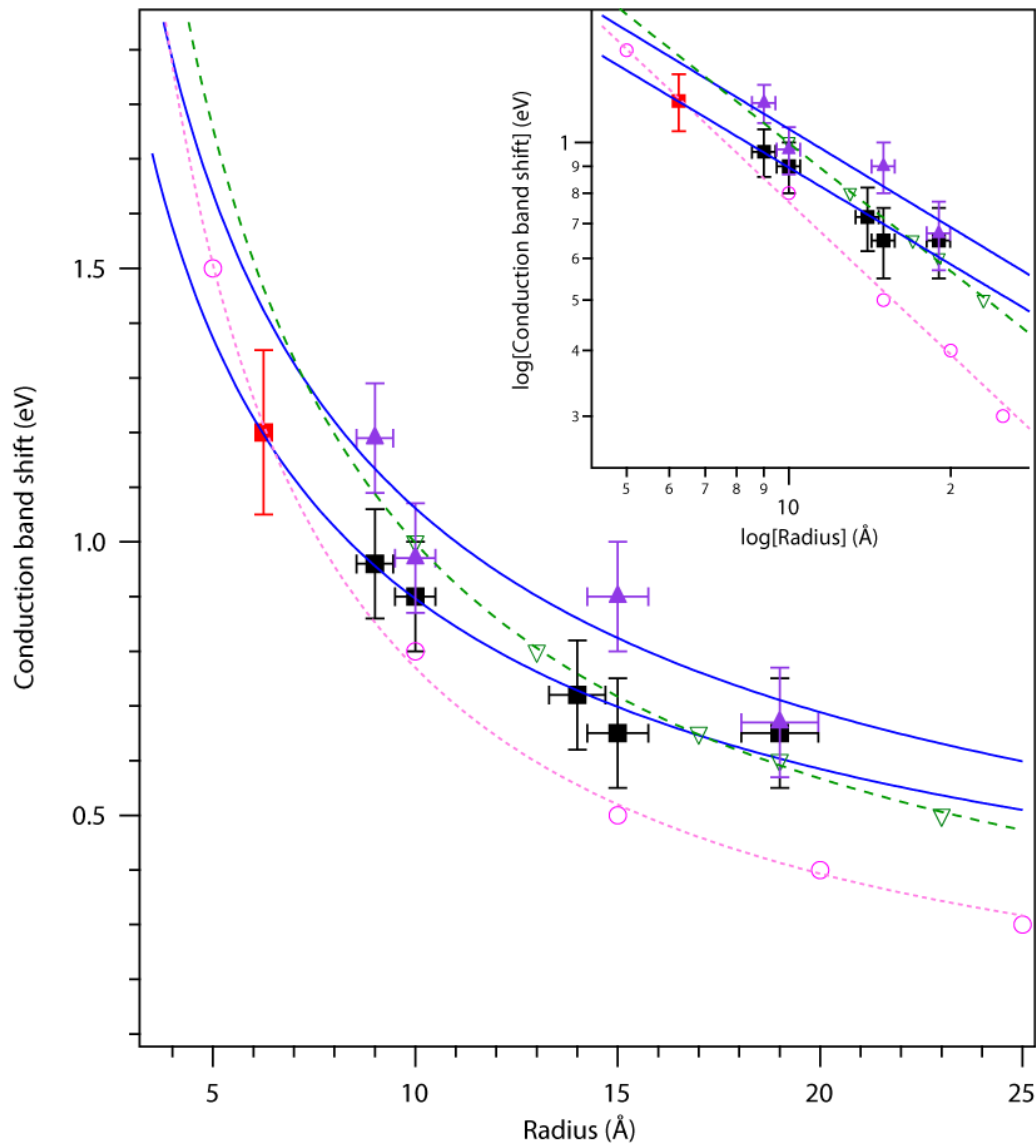


FIG. 2: Size dependent values for the CdSe conduction band states. The \square and \triangle represent the CdSe QD experimental data points using the extrapolation and arctangent subtraction data analysis methods, respectively, as described in the text, while the \circ (CP theory; Ref. 14) and ∇ (TB theory; Ref. 26) represent theoretical values. The lines through the data points represent a least squares fitting of the data. Inset: Same as A, but plotted on a Log-Log scale for better distinction between data points.

Consolidation of the plot shown in Figure 2 into a scaling law introduces a means of describing the relevant QD physics in a simple mathematical expression, which is readily compared with theoretical values. For instance, more simplistic theories like the effective mass approximation indicate that the CB shift scaling law should be, $E_c \propto R^{-2}$. More sophisticated theories like the TB method indicate the CB shift to be, $E_c \propto R^{-1.0}$. Experimentally, we observe a CB shift of, $E_c \propto R^{-0.6}$ with an error of ± 0.04 and ± 0.1 for values obtained via the extrapolation and arctangent subtraction, respectively. The scaling law obtained via the CP theory is $E_c \propto R^{-0.8}$ (see Figure 2B). The low error associated with the scaling laws allows the assertion that the experiment demonstrates better agreement with the CP theory than with the TB theory. Despite the close agreement observed in the CB scaling obtained from experiment and CP theory, the small discrepancy between the scaling laws (even with error considered) suggests new physics may occur at small sizes which slows down the shift of the CB. Therefore, we suggest that smaller exponents observed in the scaling laws are observed experimentally because a regime is entered at small sizes in which the CBM does not shift with size.

Recent results by Puzder, et al [10] suggest that small CdSe QDs (less than 10 Å radius) do not show a size dependence in the CB; rather, a consistent shift of ~ 1 eV relative to the bulk value is seen for the CBM. Although the differences between the theoretical results presented in this manuscript are difficult to explain, it has been postulated that this is in part due to differences in modeling the nanoparticle surface. We believe that the XAS results can be used to explain these contrary theoretical results in terms of a simple quantum confinement argument. The XAS results indicate that there are energy states in the upper conduction band of CdSe QDs that are inherently unaffected by quantum confinement, unlike the states at the bottom of the CB which are strongly affected. As already stated, the CdSe CBDOS are composed of Cd 5s states at the bottom of the CB, with hybridized 5p/5s state contribution above the CB minimum. In Fig. 1 it is clear that as the particle size is decreased, the s-like states shift to higher energy whereas the states labeled ps do not move. For the smallest particle size, it appears that the s states have shifted to such a degree that the bottom of the conduction band is now dominated by the hybridized p and s-like states. This would explain the contradictions between theories and suggests that the reason the CB edge no longer shifts in particles below 10 Å is that the CB minimum is now composed of hybridized p and s like states. Although Puzder et. al. argue that

surface states are responsible for the pinning of the CBM, our experiments cannot always easily resolve the differences between bulk and surface states so we are only commenting on the partial angular momentum resolved DOS, both surface and bulk. It is conceivable, therefore, that the observation of a pinned CB in our measurements may actually be related to surface states as suggested by Puzder et. al. [10]

Band structure calculations (Figure 3A and B) show that the Cd $5s$ energy bands are parabolic near the CB minimum and are expected to be highly affected by quantum confinement; the ps states are flat and should stay localized irrespective of particle size (Figure 3C) although this has not yet been explored theoretically. We have previously shown that the Cd M_5 edge, which probes p -like DOS, does not shift with particle size and only shows a size dependent broadening. [5] In the case of the $5s$ states, the observed shifts are similar to those predicted by CP theory for particles larger than ~ 10 Å radius. For particles less than 10 Å radius, the weak size dependence of the shifts indicate that the states at the conduction band minimum are most likely the flat-band ps states.

We conclude that contradictory theories in interpreting the quantum confinement induced shift of the conduction band in CdSe quantum dots can be addressed using X-ray absorption spectroscopy. As the CdSe particle size decreases, s states in the bottom of the conduction band shift to higher energy due to quantum confinement while hybridized $p/5s$ states are unaffected by size. A conduction band composed of hybridized ps states at small particle sizes is proposed. These results suggest that there exists an upper limit to extent the conduction bands of CdSe can shift with particle size and should have impact on the future fabrication of electronic materials based on CdSe.

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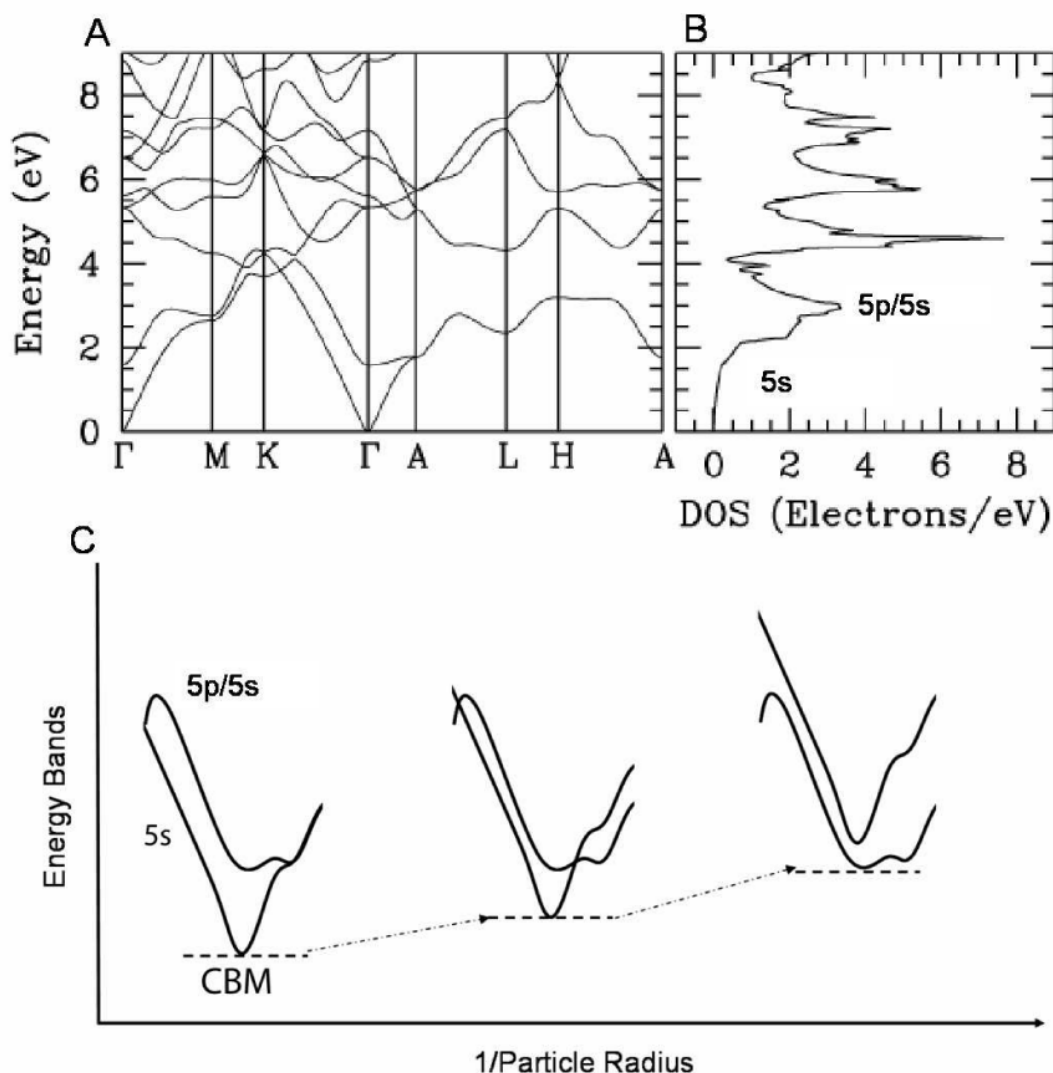


FIG. 3: (A) Calculated bulk CdSe conduction band diagram. (B) Corresponding conduction band density of states (DOS) which emphasizes the correlation of the DOS features with the energy bands. (C) Schematic energy bands depicting movement of the bands as a function of particle size. Notice the parabolic nature of the 5 s states at the conduction band minimum versus the 5 p/5 s states which explains the differences in energy shifts of the bands with quantum confinement. It must be noted that the shape of the bands as a function of particle size is not accurately represented and this illustration is intended only to demonstrate the shifts of the bands with particle size.

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